

## PATENT ABSTRACTS OF JAPAN

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**(54) ATMOSPHERIC PRESSURE PLASMA TREATMENT DEVICE, FILM MANUFACTURED BY USING THE SAME, MANUFACTURING METHOD OF FILM AND FILM MANUFACTURED BY THE SAME**

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an atmospheric pressure plasma treatment device capable of preventing an electrode from pollution and stably manufacturing a film, and to provide the film having stable quality and a manufacturing method of the same.

SOLUTION: For the atmospheric pressure plasma treatment device, forming the film on a surface of a base material by locating the base material between electrodes facing each other under an atmospheric pressure of under the pressure nearly the same as the atmospheric pressure, and by generating a discharge plasma by impressing a high frequency voltage between the electrodes under the atmosphere including reaction gas and inert gas. An exchangeable covering material is arranged at least on a part of the surface of the electrode.

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

**[Field of the Invention]**This invention relates to the film manufactured using the film production method and this film production method using the film and atmospheric pressure plasma which were manufactured using the atmospheric pressure plasma treatment apparatus and this atmospheric pressure plasma treatment apparatus.

**[0002]**

**[Description of the Prior Art]**Although it is only an example, much materials which provided the film of highly efficient nature on the substrate are used for various products, such as LSI, a semiconductor, a display device, a magnetic recording device, a photoelectric conversion device, the Josephson device, a solar cell, and a light-and-heat conversion device.

**[0003]**With the film of these highly efficient nature, for example An electrode layer, a dielectric protective film, semiconductor membrane, A transparent conducting film, an electrochromic film, a fluorescent screen, a superconductivity film, a dielectric film, A solar battery film, an antireflection film, a wear-resistant film, an optical interference film, a reflection film, an antistatic film, They are things, such as a conducting film, an antifouling film, a hard court film, an under-coating film, a barrier film, an electromagnetic wave screen, an infrared screen, an ultraviolet absorption film, lubricating film, a shape memory film, a magnetic recording film, a light emitting device film, biocompatible membrane, a corrosion-resistant film, a catalyst film, a gas sensor film, and an ornament film.

**[0004]**Conventionally, the film of such highly efficient nature is formed by the dry type producing-film method using vacuums, such as the wet producing-film method represented by spreading or sputtering process, a vacuum deposition method, and the ion plating method.

**[0005]**Since the spreading must use material which constitutes a film from a point that productivity is high although it is useful as the coating liquid dissolved or distributed to the solvent, it cannot be referred to as fit for not much highly efficient film formation -- it is difficult for the solvent concerned to remain in a film or to maintain the homogeneity of thickness. In the drying process after spreading, solvents, such as an organic solvent which evaporated from coating liquid, also include the problem of giving load to environment.

**[0006]**On the other hand, since the dry type producing-film method using the above-mentioned vacuum can form a highly precise film, it is a method desirable for forming the thin film of highly efficient nature. However,

when a processed substrate becomes large, a device enlarges dramatically the vacuum devices used for the dry type producing-film method, a price also becomes big-ticket and also the demerit that spend time and productivity is not raised is enormously large [ vacuum devices ] also to evacuation.

[0007]As a method of conquering the demerit of the underproductivity by the highly efficient film by the above and spreading using a stake demerit and vacuum devices for obtaining, Discharge under atmospheric pressure or the pressure near the atmospheric pressure, and plasma excitation of the reactive gas is carried out, The method of forming a thin film on a substrate is indicated to JP,11-133205,A, JP,2000-185362,A, JP,11-61406,A, JP,2000-147209,A, 2000-121804, etc. (it is also hereafter called an atmospheric pressure plasma process).

[0008]

[Problem(s) to be Solved by the Invention]However, since the electrode of the atmospheric pressure plasma treatment apparatus used with the atmospheric pressure plasma processing method indicated by the above-mentioned gazette is a fixed electrode, Since it is exposed to the discharge plasma which always has film production nature, the electrode is polluted with time progress, change of an inter-electrode discharge gap arises owing to this contamination, and it has the problem of giving variation to the character of the film formed in a substrate.

[0009]An electrode will especially be polluted with ultrashort time amount from the speed of the film production speed at an atmospheric pressure plasma process. In atmospheric pressure plasma in recent years, since the inter-electrode gap is narrowed, inter-electrode plugging may arise with the dirt of an electrode.

[0010]This invention is made in view of this technical problem, and is a thing.

The purpose is to provide the atmospheric pressure plasma treatment apparatus and the film production method of preventing the dirt of an electrode and producing a film by being stabilized, and the film which has the stable quality further.

[0011]

[Means for Solving the Problem]The purpose of this invention was attained by the following composition.

[0012](1) A substrate is located in inter-electrode [ which counters under atmospheric pressure or a pressure near the atmospheric pressure ], In an atmospheric pressure plasma treatment apparatus which generates discharge plasma and forms a film in the surface of said substrate by making a gas which furthermore contains reactant gas and inactive gas exist, and impressing high frequency voltage to inter-electrode [ said ], An atmospheric pressure plasma treatment apparatus providing a coating of the surface of said electrode exchangeable at least in part.

[0013](2) An atmospheric pressure plasma treatment apparatus given in (1) which locates said substrate so that at least a part of one electrode surface of said electrode which counters may be covered, and is characterized by a thing of an electrode surface of another side established for said coating in part at least.

[0014](3) (1), wherein said coating is heat resistant resin, or an atmospheric pressure plasma treatment apparatus given in (2).

[0015](4) An atmospheric pressure plasma treatment apparatus given in any 1 paragraph of (1) - (3), wherein said coating contains polyimide.

[0016](5) An atmospheric pressure plasma treatment apparatus given in any 1 paragraph of (1) - (4), wherein said coating contains fluoro-resin.

[0017](6) An atmospheric pressure plasma treatment apparatus given in any 1 paragraph of (1) - (5), wherein thickness of said coating is 1 micrometer - 2000 micrometers.

[0018](7) An atmospheric pressure plasma treatment apparatus given in any 1 paragraph of (1) - (6), wherein it has a coating means of exchange which exchanges said coating and said coating means of exchange has a means which lets out said coating, and a means which rolls round said coating.

[0019](8) An atmospheric pressure plasma treatment apparatus given in any 1 paragraph of (1) - (6), wherein it is possible to have pasted up said coating and said electrode with a binder, and to remove and exchange said coating.

[0020](9) An atmospheric pressure plasma treatment apparatus given in (8), wherein said binder contains a compound of acrylic or a silicon system.

[0021](10) (1) Film manufactured using an atmospheric pressure plasma treatment apparatus of a statement in any 1 paragraph of - (9).

[0022](11) A substrate is located in inter-electrode [ which counters under atmospheric pressure or a pressure near the atmospheric pressure ], In a film production method which generates discharge plasma and forms a film in the surface of said substrate by making a gas which furthermore contains reactant gas and inactive gas exist, and impressing high frequency voltage to inter-electrode [ said ], A film production method providing a coating of an electrode surface of said electrode which counters exchangeable at least in part.

[0023](12) said substrate -- at least a part of one electrode surface of said electrode which counters -- a wrap -- you make it located like -- said exchangeable coating -- at least a part of electrode surface of another side of said electrode which counters -- a wrap -- a film production method given in (11) making it like.

[0024](13) (11), wherein said coating is heat resistant resin, or a film production method given in (12).

[0025](14) A film production method given in any 1 paragraph of (11) - (13), wherein said coating contains polyimide.

[0026](15) A film production method given in any 1 paragraph of (11) - (14), wherein said coating contains fluoro-resin.

[0027](16) A film production method given in any 1 paragraph of (11) - (15), wherein thickness of said coating is 1 micrometer - 2000 micrometers.

[0028](17) A film production method given in any 1 paragraph of (11) - (16) rolling round said coating and exchanging by a method.

[0029](18) A film production method given in any 1 paragraph of (11) - (16) having pasted up said coating and said electrode with a binder, and removing and exchanging said coating.

[0030](19) A film production method given in (18), wherein said binder contains a compound of acrylic or a silicon system.

[0031](20) (11) Film manufactured using a film production method of a statement in any 1 paragraph of - (19).

[0032]This invention is explained in detail below. This invention persons are providing a coating of the surface of an electrode which counters in order to prevent dirt of an electrode exchangeable at least in part,

and found out preventing contamination of an electrode. It found out that a film could be produced by being stabilized by exchanging a coating for a new coating if dirt adheres to a coating.

[0033]In this invention, it is an electrode which counters and it is preferred to provide a coating in all portions exposed to discharge plasma. Thereby, dirt of an electrode can be pressed down nearly thoroughly.

[0034]Case [ like an atmospheric pressure plasma treatment apparatus which produces a film with structure where a substrate located in inter-electrode / which counters / covers a part of electrode surface ], it is not necessary to provide a coating in an electrode surface portion covered with a substrate.

[0035]In this invention, the bottom of atmospheric pressure or a pressure near the atmospheric pressure is under a pressure of 20kPa - 110kPa. In this invention, inter-electrode still more desirable pressures which impress voltage are 93kPa - 104kPa.

[0036]

[Embodiment of the Invention]Although a figure is used for below and the embodiment is described to it about the atmospheric pressure plasma treatment apparatus and the film production method of this invention, this invention is not limited to this. Although the affirmative expression to a term etc. may be included in the following explanation, the desirable example of this invention is shown and a terminological meaning or technical range of this invention are not limited.

[0037]Drawing 1 is a sectional view showing an example of the atmospheric pressure plasma treatment apparatus of this invention. 1 is a substrate. Although the construction material of the substrate processed with the atmospheric pressure plasma treatment apparatus of this invention does not have limitation in particular, cellulose ester bases, such as cellulose triacetate, a polyester base, a polycarbonate base, a polystyrene base, a polyolefine base, a glass substrate, etc. can be processed.

[0038]Specifically Polyester, such as polyethylene terephthalate and polyethylenenaphthalate, Polyethylene, polypropylene, cellophane, cellulose diacetate, Cellulose acetate butylate, cellulose acetate propionate, Cellulose ester or those derivatives, such as cellulose acetate phthalate, cellulose triacetate, and nitrocellulose, A polyvinylidene chloride, polyvinyl alcohol, ethylene vinyl alcohol, A syndiotactic polystyrene system, polycarbonate, norbornene resin, A polymethylpentene, polyether ketone, polyimide, polyether sulphone, a polysulfone system, polyether ketoneimide, polyamide, a fluoro-resin, nylon, polymethylmethacrylate, an acrylic, or polyarylate can be mentioned. these raw materials are independent -- it is -- it can also be used, being mixed suitably. Commercial items, such as ZEONEX (made by Nippon Zeon Co., Ltd.) and ARTON (made by Japan Synthetic Rubber Co., Ltd.), can be used especially.

[0039]2 and 3 are electrodes, and the electrode 2 and the electrode 3 counter and are installed. The electrodes 2 and 3 have covered the dielectric and this dielectric carries out sealing of the spraying film of aluminum<sub>2</sub>O<sub>3</sub> ceramics by alkoxysilane.

[0040]As for the electrode used for the atmospheric pressure plasma treatment apparatus of this invention, it is preferred that at least one electrode is covered with the dielectric. Metal, such as silver, platinum, stainless steel, aluminum, and iron, can be used for an electrode material. Stainless steel can be used preferably that it is easy to process it. As a dielectric, silicate system glass borate system glass phosphate system glass germane acid chloride system glass, tellurite glass aluminate glass vanadate glass, etc. can be used. Also in this, it is easy to process borate system glass. It is also preferred to use the ceramics which

sintered the ceramics of airtight high heat resistance. Although the ceramics of an alumina system, a zirconia system, a silicon nitride system, and a silicon carbide system are mentioned as construction material of ceramics, the ceramics of an alumina system are especially preferred and it is preferred to use aluminum<sub>2</sub>O<sub>3</sub> also especially in the ceramics of an alumina system. As for the thickness of the ceramics of an alumina system, about 1 mm is preferred, and more than 10<sup>8</sup> ohm-cm of volume resistivity is preferred.

[0041]As for ceramics, it can be preferred that sealing is carried out with the inorganic material, and, thereby, it can raise the endurance of an electrode.

[0042]Sealing can carry out sealing of ceramics with the metallic oxide which makes a firm three-dimensional combination form and has a uniform structure by making it gel and making it harden, after applying to ceramics on ceramics the sol which uses as the main raw material the metal alkoxide which is sealer.

[0043]In order to promote a sol gel reaction, it is preferred to perform energy processing. Specifically, three-dimensional combination of metal-oxygen-metal can be promoted by carrying out energy processing to sol.

[0044]To energy processing, plasma treatment, and heat-treatment at 200 °C or less and UV processing are preferred.

[0045]As for having a means to perform ~~temperature control~~ of the ~~electrodes 2 and 3~~, to the electrodes 2 and 3, it is preferred to pour incubation water in an electrode etc.

[0046]On the electrode 3, the atmospheric pressure plasma treatment apparatus shown in drawing 1 arranges the ~~substrate 1~~, and performs atmospheric pressure plasma treatment. The electrode 3 is horizontally ~~movable~~ and has structure whose reciprocating movement is possible. Discharge plasma can be uniformly exposed to the surface of the substrate 1 by this, and a uniform film can be formed in the surface of the substrate 1.

[0047]~~4 is a coating. The coating is provided in order to prevent polluting the electrode 2.~~

[0048]As for the coating 4, it is preferred that it is heat resistant resin. The coating 4 is arranged in the electrode of an atmospheric pressure plasma treatment apparatus at a wrap position. It is because it serves as an elevated temperature dramatically while the electrode is performing atmospheric pressure plasma treatment, and the coating 4 can bear this high temperature state. The heat resistant resin as used in the field of this invention refers to the thing of resin which has the heat resistance of not less than 150 °C, and refers to the thing of resin which has the heat resistance of not less than 200 °C preferably.

[0049]As for the coating 4, it is preferred to contain ~~polyimide~~. Thereby, the heat resistance of the coating 4 can be raised.

[0050]As for the coating 4, it is preferred to contain ~~fluororesin~~. Thereby, the heat resistance of the coating 4 can be raised.

[0051]As for the coating 4, it is preferred that thickness is 1-2000 micrometers. By considering it as this range, generating of plasma discharge is not affected, it is stabilized and atmospheric pressure plasma treatment can be performed.

[0052]The coating 4 serves as ~~shielded state~~ by which the binder was applied to the rear face, and is arranged in the state where it stuck on the electrode 3. The coating 4 is polluted with doing in this way, when

uninfluential [ appearing in atmospheric pressure plasma treatment ], the coating 4 can be removed and atmospheric pressure plasma treatment can be stably performed by sticking the new coating 4.

[0053]At this time, since the binder used for the coating 4 touches an electrode, it is preferred to have the heat resistance of not less than 150 \*\*.

[0054]It is preferred to contain the compound of acrylic or a silicon system in a binder. Thereby, the heat resistance of a binder can be raised.

[0055]As the coating 4 used by this invention, the Scotch whisky Kapton tapes 5412, 5413-5451, 5453, 5480, 5490, and 5491 (made by Sumitomo 3M), The tape of marketing of a polyimide tape (made by NITTO DENKO CORP.), a polyimide tape (made in [ shrine ] transformation [ Restoration ]), a polyimide tape (made by a permanent wave cell company), a PEFE tape (made in [ shrine ] transformation [ Restoration ]), etc. can be used preferably.

[0056]A coating continues and enables it to perform atmospheric pressure plasma treatment stably in this invention by exchanging coatings, when it is provided in order to prevent the dirt by the discharge plasma of an electrode, and a coating becomes dirty. Therefore, as for a coating, it is preferred that clearing work is the structure which becomes easy. In the atmospheric pressure plasma treatment apparatus given in drawing 1, the coating 4 is made into shielded state and clearing work is made easy by considering it as the structure which can be stuck on the electrode 2 or can be removed. The clearing work of a coating may be manual, or may be automatic, and it is preferred to choose suitably in consideration of the advancing state of contamination of a coating, the structure of an atmospheric pressure plasma treatment apparatus, etc.

[0057]5 is an RF generator for impressing the high-frequency voltage of 100 Hz - 150 MHz between the electrodes 2 and 3. 6 is a ground and the electrode 3 is grounded to the ground 6. As for RF generator 5, it is preferred that discharge outputs are  $1 \text{ W/cm}^2 - 50 \text{ W/[cm]}^2$ , and, thereby, it can raise the plasma density of discharge plasma more.

[0058]The atmospheric pressure plasma treatment apparatus shown in drawing 1 impresses high frequency voltage between the electrodes 2 and 3 in the state where the gas containing reactant gas and inactive gas was made to exist between the electrodes 2 and 3.

[0059]As reactant gas used for this invention, an organic fluorine compound and metallic compounds can be mentioned preferably. A useful low refractive index layer and stain-proofing barrier can be formed in an antireflection layer etc. by using an organic fluorine compound. In metallic compounds, a low refractive index layer, a medium refractive index layer, a high refractive index layer, a gas barrier layer, an antistatic layer, and also a transparent conductive layer can be formed.

[0060]As an organic fluorine compound, gas, such as carbon fluoride, hydrocarbon, fluoridation, is preferred, For example, methane fluoridation and ethane fluoridation, tetrafluoromethane, hexafluoroethane, 1,1,2,2-tetrafluoroethylene, 1,1,1,2,3,3-hexafluoropropane, Carbon fluoride compound; 1,1-difluoroethylene, such as 6-hexafluoro propene, propylene, fluoridation, Fluoridation hydrocarbon compounds, such as 1,1,1,2-tetrafluoro ethane and 1,1,2,2,3-pentafluoropropane; Difluorodichloromethane, Fluoride salt carbonizing-ized hydride; 1, such as trifluorochloromethane, 1, 1, 3 and 3, 3-hexafluoro 2-propanol, Fluoridation alcoholic [, such as 1,3-difluoro-2-propanol and perfluoro butanol ]; Vinyl trifluoroacetate, Fluoridation carboxylate, such as 1,1,1-trifluoroethyl trifluoroacetate; although ketone fluoridation, such as acetyl fluoride,



hexafluoroacetone, and 1,1,1-trifluoroacetone, can be mentioned, it is not limited to these.

[0061]Although it is preferred that an organic fluorine compound chooses a compound which corrosive gas or harmful gas does not generate by plasma discharge processing, the conditions which they do not generate can also be chosen. When using an organic fluorine compound for this invention as useful reactive gas, it can be used as it is as most suitable reactive gas ingredient for that an organic fluorine compound is a gas to carry out the purpose, and is desirable at ordinary temperature ordinary pressure. On the other hand, by ordinary temperature ordinary pressure, what is necessary is just to use it, evaporating by vaporizers, such as heating and decompression, or other means, and may dissolve in a suitable organic solvent, and it is made to spray or evaporate in the case of the organic fluorine compound of a fluid or a solid, and may use for it.

[0062]As metallic compounds, aluminum, As, Au, B, Bi, Ca, Cd, Cr, Co, Cu, Fe, Ga, germanium, Hg, In, Li, Mg, Mn, Mo, Although metallic compounds or organic metallic compounds, such as Na, nickel, Pb, Pt, Rh, Sb, Se, Si, Sn, Ti, V, W, Y, Zn, or Zr, can be mentioned and aluminum, germanium, In, Sb, Si, Sn, Ti, W, Zn, or Zr is preferably used as metallic compounds, In particular, a silicon compound, a titanium compound, a tin compound, a zinc compound, an indium compound, an aluminum compound, a copper compound, and a silver compound are preferred.

[0063]As a silicon compound, among these, for example Dimethylsilane, a tetramethylsilane, Alkyl silanes, such as a tetraethyl silane; A tetramethoxy silane, a tetraethoxysilane, Tetra propoxysilane, dimethyl diethoxysilane, methyl trimetoxysilane, Organosilicon compounds, such as silicon alkoxides, such as ethyltriethoxysilane; A mono silane, silicon hydride [, such as a disilane, ]; -- silicon halide compound [, such as a dichloro silane, trichlorosilane, and tetrachlorosilane, ]; -- in addition to this, an organosilane etc. can be mentioned and all can be used preferably. These can be combined suitably and can be used. The silicon alkoxide from a viewpoint on handling, an alkyl silane, and the organic silicon hydride are preferred, the above-mentioned organosilicon compound does not have generating of corrosiveness and harmful gas, and its silicon alkoxide is preferred especially as an organosilicon compound from there being little dirt on a process, etc.

[0064]As a titanium compound, a tin compound, a zinc compound, an indium compound, an aluminum compound, a copper compound, and a silver compound, an organic metallic compound, halogenation metallic compounds, metal hydride, and a metal alkoxide compound are preferred. As an organic component of an organic metallic compound, an alkyl group, an alkoxide group, and an amino group are preferred, and can mention preferably tetraethoxytitanium, tetrakispropoxy titanium, tetrabutoxytitanium, tetra dimethylamino titanium, etc. An organic titanium compound, an organic tin compound, an organozinc compound, the organic indium compound, the organic aluminum compound, the organocopper compound, and the organic silver compound are dramatically useful although a medium refractive index layer and a high refractive index layer are formed. As halogenation metallic compounds, a titanium dichloride, titanium trichloride, titanium tetrachloride, etc. can be mentioned, and also monotitanium, JICHITAN, etc. can be mentioned as metal hydride. In this invention, the organic metallic compound of a titanium system can be used preferably.

[0065]In this invention, although it is preferred that they are 0.01 volume % - 10 volume % as for the rate of the reactant gas occupied in a gas, they are 0.1 volume % - 5 volume % still more preferably.



[0066]As inactive gas, as for the rate of the inactive gas occupied in a gas, although rare gas, such as helium and Ar, is used preferably, the rare gas which mixed helium and Ar is also preferred, and it is preferred that they are 90 volume % - 99.9 volume %. Although it is also preferred to increase the Ar gas ingredient in inactive gas from the point of generating atmospheric pressure plasma efficiently, it is preferred to use 90 volume % - 99.9 volume % for an Ar gas ingredient also from a viewpoint of cost.

[0067]It may be used for it, making inactive gas able to do 0.1 volume %-10 volume % mixing of hydrogen gas or oxygen gas to inactive gas, and the hardness of a thin film can be remarkably raised by using it auxiliary in this way.

[0068]Although plasma discharge is used as a means to excite a gas, in the atmospheric pressure plasma treatment apparatus explained by this embodiment, as a means to excite a gas, there are means other than plasma discharge, such as electron beam irradiation, radiation irradiation, UV irradiation, and flame radiation.

[0069]Next, the atmospheric pressure plasma processing method using the atmospheric pressure plasma treatment apparatus shown in drawing 1 is explained.

[0070]The substrate 1 is arranged on the electrode 3. The arranged substrate 1 is arranged so that the surface of the electrode 3 may be covered.

[0071]~~The gas containing reactant gas and inactive gas~~ is made to exist between the electrodes 2 and 3. The high frequency voltage of 100 Hz - 150 MHz is impressed to the gas which exists between the electrodes 2 and 3 by RF generator 5 under atmospheric pressure or the pressure near the atmospheric pressure, discharge plasma is generated, ~~and a film is produced on the surface of the substrate 1 by this discharge plasma. The electrode 3 repeats reciprocation moving horizontally in the midst of plasma treatment, and let the film formed in the substrate 1 be a uniform thing. After forming a film in the substrate 1, the following substrate 1 is arranged on the electrode 3, and the film is similarly formed on the substrate 1. If a film is formed in some substrates, the coating 4 which has covered the electrode 2 will be polluted by discharge plasma. When judged as the state where the film production to the substrate 1 is affected by the influence of contamination of the coating 4, the coating 4 is removed, the new coating 4 is stuck, and it enables it to produce the substrate 1 stably under it.~~

[0072]Drawing 2 is a sectional view showing other examples of the atmospheric pressure plasma treatment apparatus of this invention. In explanation of drawing 2, although it may be omitted about explanation of the thing of the same numerals as the numerals explained by the above-mentioned description of drawing, and the explanation relevant to it, as long as there is no explanation in particular, it is the same as the above-mentioned description of drawing.

[0073]The atmospheric pressure plasma treatment apparatus shown in drawing 2 differs from the atmospheric pressure plasma treatment apparatus shown in drawing 1 in respect of the exchange method of the coating 4.

[0074]~~4a is a coating delivery means which lets out the coating 4. 4b is a coating rolling means which rolls round the coating 4.~~

[0075]The electrode 2 of the atmospheric pressure plasma treatment apparatus shown in drawing 2 is covered with the coating 4, and ~~prevents dirt adhering to the electrode 2 by atmospheric pressure plasma treatment by this.~~

[0076]Next, the atmospheric pressure plasma processing method using the atmospheric pressure plasma treatment apparatus shown in drawing 2 is explained.

[0077]The substrate 1 is arranged on the electrode 3. The arranged substrate 1 is arranged so that the surface of the electrode 3 may be covered.

[0078]The gas containing reactant gas and inactive gas is made to exist between the electrodes 2 and 3. The high frequency voltage of 100 Hz - 150 MHz is impressed to the gas which exists between the electrodes 2 and 3 by RF generator 5 under atmospheric pressure or the pressure near the atmospheric pressure, discharge plasma is generated, and a film is produced on the surface of the substrate 1 by this discharge plasma. ~~The electrode 3 repeats reciprocation moving horizontally in the midst of plasma treatment, and let the film formed in the substrate 1 be a uniform thing. After forming a film in the substrate 1, the following substrate 1 is arranged on the electrode 3, and the film is similarly formed on the substrate 1. If a film is formed in some substrates, the coating 4 which has covered the electrode 2 will be polluted by discharge plasma. When judged as the state where the film production to the substrate 1 is affected by the influence of contamination of the coating 4, It lets out the new coating 4 by the coating delivery means 4a, as the coating 4 polluted by the coating rolling means 4b is rolled round further, the coating 4 is exchanged, and it enables it to produce the substrate 1 stably.~~

[0079]Drawing 3 is a sectional view showing other examples of the atmospheric pressure plasma treatment apparatus of this invention. The electrode 3a of two or more prismatic cover halves is made to counter in drawing 3 to the electrode 2a of the forging roll die which winds the substrate 1 and carries out conveyance rotation. Metal, a dielectric, etc. which are used by the electrode of drawing 1 and the atmospheric pressure plasma treatment apparatus of 2 can be used for the electrodes 2a and 3a.

[0080]The atmospheric pressure plasma treatment apparatus shown in drawing 3 is a device which can perform film production processing succeeding a case so that a film may be produced on the surface of the substrate of film state.

[0081]the electrode 3a of a prismatic cover half -- each is covered by the coating 4. the coating 4 has adhesives at the rear face -- the electrode 3a -- it is alike, respectively and is stuck. Since electrode dirt is a portion which does not happen comparatively easily, it may be made stick the coating 4 so that all the surface parts of the electrode 3a may be covered, but for the reverse part and lateral portion of the electrode 3a to form the coating 4 only in the front part of the electrode 3a according to a situation.

[0082]Next, the atmospheric pressure plasma processing method using the atmospheric pressure plasma treatment apparatus shown in drawing 3 is explained.

[0083]On the electrode 2a, the substrate 1 is arranged so that a roll side may be touched. The arranged substrate 1 is arranged so that the surface of the electrode 2a may be covered.

[0084]The gas containing reactant gas and inactive gas is made to exist between the electrode 2a and 3a. The high frequency voltage of 100 Hz - 150 MHz is impressed to the electrode 2a and the gas which exists among 3a by RF generator 5 under atmospheric pressure or the pressure near the atmospheric pressure, discharge plasma is generated, and a film is produced on the surface of the substrate 1 by this discharge plasma. The substrate 1 has the electrode 2a top conveyed, and produces the surface of the substrate 1 continuously. If the film is continuously produced to the substrate 1, the coating 4 which has covered the electrode 2a will be polluted by discharge plasma. When judged as the state where the film production to the

substrate 1 is affected by the influence of contamination of the coating 4, the coating 4 is removed, the new coating 4 is stuck, and it enables it to produce the substrate 1 stably under it.

[0085]

[Example] Hereafter, although an example explains this invention concretely, this invention is not limited to these.

[0086] Example 1 It experimented using the atmospheric pressure plasma treatment apparatus shown in film production processing example 1-1 drawing 1.

[0087] The electrodes 2 and 3 of drawing 1 use stainless steel SUS316 for an electrode, and it further, The coating liquid made to dissolve alkoxysilane monomer in an organic solvent after carrying out flame spraying of the alumina ceramic on the surface of an electrode until it is set to 1 mm was applied to the alumina ceramic tunic, after making it dry, it heated at 150 \*\*, sealing was performed, and the dielectric was formed. Connection of RF generator 5 and grounding of the ground 6 were performed into the portion which has not covered the dielectric of the electrodes 2 and 3. It enabled it to circulate through incubation water in the electrode 2 and 3 furthermore.

[0088] The 80-micrometer-thick polyimide tape (the Sumitomo 3M make, the Scotch whisky Kapton tape 5413, 80 micrometers) was stuck on the electrode 2 as the coating 4.

[0089] The gas A and the gas B were used for the reactant gas and inactive gas which are introduced between the electrodes 2 and 3.

[0090] Gas A: argon gas 98.5% and 1.5% of hydrogen gas gas B: tetraethoxysilane 0.3%, and argon gas 99.7% (a tetraethoxysilane is evaporated in argon gas with the vaporizer by S-Tec Co., Ltd.)

The gas A and B was supplied at a rate of 2:1.

[0091] Continuation frequency was set to RF generator 5 at 2 MHz using the RF generator made from pearl industry, and the discharge output of  $10 \text{ W/cm}^2$  was impressed between the electrodes 2 and 3. The distance between the electrodes 2 and 3 was set as 3 mm.

[0092] The film was produced by arranging using a 2-mm-thick glass base material as the substrate 1, so that the surface of the electrode 3 may be covered. Film production was completed when membranous thickness was set to 100 nm.

[0093] In the stage which produced the film to a total of 20 substrates, the polyimide tape was again stuck on a new polyimide tape, film production processing was continued, and a total of 100 substrates were produced.

[0094] In one to example 2 Example 1-1, the film was produced to a total of 100 substrates like Example 1-1 except not having covered the electrode 2 with a polyimide tape.

[0095] In one to example 3 Example 1-1, the film was produced to a total of 100 substrates like Example 1-1 except having changed into the vinyl tape ( anchor brand by TERAOKA) the coating 4 stuck on the electrode 2.

[0096] In one to example 4 Example 1-1, the coating 4 stuck on the electrode 2 was produced to a total of 100 substrates like Example 1-1 except having piled up five polyimide tapes.

[0097] Example 2 The following classification estimated the film production situation of 100 substrates which produced the film in each soiled state and each example of the electrodes 2 and 3 of the atmospheric

pressure plasma treatment apparatus after producing a film to 100 substrates used in evaluation example 1-1 to 1-4. A result is shown in Table 1.

O : -- the substrate with which x:film production to which film production is uniform about 80-94 O:substrates with which film production is uniform about 95-100 substrates, and film production is performed correctly, and film production is performed correctly is uniform, and film production is performed correctly -- 79 or less pieces [0098]

[Table 1]

実施例	電極汚れ	基材の製膜評価
1-1	電極の直接汚れなし	◎
1-2	電極2の汚れあり	×
1-3	電極の直接汚れなし	○
1-4	電極の直接汚れなし	○

[0099]From the result of Table 1, electrode dirt did not generate the device which produced the film by Example 1-1, 1-3, and 1-4. This is because the coating 4 is formed in the electrode. The substrate which produced the film in Example 1-1 was understood that especially the film formed in a substrate is uniform, and exact. This is the thickness of the range to which the coating used in Example 1-1 does not affect inter-electrode discharge greatly.

Since it was the construction material which furthermore does not cause degradation with the heat of discharge, it is thought that it is because plasma treatment was performed correctly.

[0100]

[Effect of the Invention]The atmospheric pressure plasma treatment apparatus and the film production method of producing a film by preventing the dirt of an electrode and being stabilized by this invention, and the film which has the stable quality further were able to be provided.

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[Translation done.]

**\* NOTICES \***

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- 1.This document has been translated by computer. So the translation may not reflect the original precisely.
- 2.\*\*\*\* shows the word which can not be translated.
- 3.In the drawings, any words are not translated.

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**DESCRIPTION OF DRAWINGS**

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[Brief Description of the Drawings]

[Drawing 1]It is a sectional view showing an example of the atmospheric pressure plasma treatment apparatus of this invention.

[Drawing 2]It is a sectional view showing other examples of the atmospheric pressure plasma treatment apparatus of this invention.

[Drawing 3]It is a sectional view showing other examples of the atmospheric pressure plasma treatment apparatus of this invention.

[Description of Notations]

1 Substrate

2, 3, 2a, and 3a Electrode

4 Coating

4a Coating delivery means

4b Coating rolling means

5 RF generator

6 Ground

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[Translation done.]